

Process for producing a fibrous composition

The present invention concerns a process for producing a fibrous composition in accordance with the preamble of claim 1.

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Such a composition generally comprises porous fibres of plant origin, as well as synthetic, electrically conductive polymers and it is produced through polymerization of electrically conductive polymers within fibres.

10 Paper and paper products, which contain electrically conductive polymers, are known from the patent literature. Thus, US Patent Specification No. 5,421,959 discloses a composite consisting of paper and an electrically conductive polymer, which is suitable for use e.g. as an electrode in primary or secondary batteries, as an antistatic packaging material and in products shielding against electromagnetic radiation. The composite is manufactured by
15 immersing the paper into a solution, which contains a precursor of an electrically conductive, conjugated polymer, which is then impregnated into the paper, the paper subsequently being heat treated in order to form a polymer on the surface of the paper.

DE Published Patent Application No. 19826800 discloses a security paper, which contains
20 rodlike pigments or transparent polymers, which are electrically conducting. The pigments or the polymers can be mixed into the paper by adding them to the furnish in the headbox of a paper machine in order to evenly distribute them throughout the paper pulp.

A wallpaper which protects against radiomagnetic radiation is presented in EP Published
25 Patent Application 1 139 710, said wallpaper being manufactured by coating a wallpaper with a mixture containing a matrix polymer, an electrically conductive polymer and additive components mixed with these.

In the known paper products, the polymers are rather loosely attached to the fibrous matrix.
30 When the polymer is mechanically mixed with the fibers, the attachment of the polymer to the fibres is weak, because the polymer is generally hydrophobic and the fibres are hydrophilic. By polymerizing a precursor impregnated into the paper, the polymer is precipitated primarily on top of the fibres because there is only small penetration of the precursor into the ready-made fibrous matrix of the paper, which means that

polymerization takes place on the surface of the fibrous matrix. And then again, when a paper is coated with a layer, which contains an electrically conductive polymer, the electrically conductive polymer does not bond directly to the cellulosic fibres but rather to the matrix polymer, whereby the electrically conductive polymer remains on the surface of the product and is released therefrom together with the coating colour. In connection with the present invention, we have found that it is important for the practical production process and for the use of the products that the electrically conductive polymer attaches firmly to the cellulosic fibres. Any polymer released from the fibres will impair the recovery and recycling of the aqueous circulation flows on a paper machine and, consequently, will weaken the functionality of the product in due course. Furthermore, it would be preferable to introduce the conductive polymer into the fibrous product directly during the production process. Hence, it is sensible from a technical point of view to manufacture electrically conductive paper or cardboard on a paper machine only if the polymer has attached to the fibres firmly enough to avoid a reduction in conductivity below the detection limit at the conditions prevailing in the paper machine due to washout of the polymer.

US Patent Specification No. 5,211,810 discloses a package which can be used for frying in microwave ovens, containing fibres having an electrically conductive polymer deposited on the surface thereof. The polymerization is carried out *in situ* in the presence of a strong mineral acid, viz. 1 N hydrochloric acid. There is no mention in the publication of the electrical conductivity of the fibres or of the products manufactured therefrom.

Even this known solution exhibits considerable disadvantages. Thus, as a consequence of the polymerization conditions, a significant part of the polymer becomes homopolymerized in the solution. This homopolymer will separate from the reaction mixture. At the conditions described in the US Patent, the low pH of the mineral acid will further be detrimental to the properties of cellulosic and lignocellulosic fibres. The acid will, therefore, modify, for example the amorphous regions of cellulose. When pH drops below 2, the strength potential of the fibrous product is significantly lowered. A low pH will keratinize the fibre and the water retention capacity of the fibre is impaired. Such a keratinized fibre also requires considerably much more beating energy. The fibres are also stiffer. A treatment at low pH is almost comparable to drying of the cellulosic pulp.

The invention aims at providing a paper or cardboard product of a novel kind, containing electrically conductive polymers, which are attached to the fibre network so firmly that they are not substantially out-washable. In the present invention, this means that the electrical conductivity of the product can be recovered even though it might decrease temporarily while a doping agent dissolves during wet cleaning.

According to the invention, a polymer is attached to free, porous natural fibres before the formation of a fibrous web from them on a paper or a cardboard machine. The composition can be produced in a way that porous fibres are brought in close contact with an electrically conductive polymer, in an aqueous intermediate agent and then, the electrically conductive polymers are allowed to attach to the fibres, resulting in a fibre composition where the polymer is so firmly attached to the fibres that it cannot be substantially washed out by water. If desired, the fibre composition is recovered.

In the process according to the invention, the polymerization of the electrically conductive polymer is carried out "*in situ*" in porous fibres. This is achieved first by impregnating both the monomer to be polymerized and a doping agent of the conductive polymer into porous fibres and then allowing these to form a salt. Thereafter, a catalyst or an oxidative agent enabling a polymerization reaction is added resulting in polymerization of the doped monomer inside the fibres and on the top of the fibres as well as in attachment of the monomer to the fibres. It is essential to the invention that the doping agent to be used is an organic sulphonic acid, which is first allowed to impregnate into the fibres to be treated, and thereafter, a monomer corresponding to the polymer is introduced to the reaction mixture and this monomer is polymerized and attached to the surfaces of the fibres and, especially, inside the fibres.

More specifically, the process according to the invention is characterized by what is stated in the characterizing part of claim 1.

Considerable advantages are obtained by means of the invention. Hence, a mixture that can be used to form a conductive network in a paper and a cardboard web can be built up by the invention. By adjusting the amount of the electrically conductive polymer, a selected level of conductivity can be reached, ranging e.g. from 10^4 to 10^{11} ohm/square and typically from about 10^4 to 10^8 ohm/square. It is easy to distinguish the product from a

non-conductive product when the square resistance is equal to or less than 10^8 . Multiple different kinds of functions can be achieved by including a conductive network into paper or cardboard, these functions being connected to antistatic applications, entering identification data, security markings etc. depending on their level of conductivity.

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In particular, the present invention provides a fibrous product having an electrical conductivity, which is maintained over extended periods of time and retention, which is good on a wire. In connection with the composition and the production of the fibre web, respectively, only a small amount of a non-adhesive polymer is transferred to waste and
10 circulation water.

When the electrically conductive polymer is firmly attached to the fibres, for example already in the headbox of the paper machine, the polymer becomes evenly and homogeneously distributed throughout the entire paper furnish. This has the advantage that
15 proper conductivity is reached at a lower amount of polymer than in a situation where the polymer is present between the fibres, e.g. in dispersed form. As indicated in the examples below, good conductivity of about 10^4 Ohm can already be reached by a total of 10 weight-% of polyaniline (of the pulp).

20 It is known from EP Published Patent Application 0 783 015 to coat microfibrils with polypyrrole. The size of such fibrils is on the order of micrometres and their diameter is usually 2 to 30 nanometres. According to the present invention, microfibrils are not, however, modified but natural fibres, i.e. "vegetable fibres", such as cellulosic or lignocellulosic fibres. The structure of fibres of this kind is usually comprised of five
25 different wall layers and their length in softwood is typically about 3 mm. The layers of the walls contain ligning, hemicellulose and cellulose. Of these components, the cellulose molecules are bonded to each other by hydrogen bonds forming short microfibrils, which in turn are organized as bunches and form fibrils which are orientated in different directions in the various fibres wall layers. In the present invention, the conductive
30 polymer has penetrated into the fibres.

Modified cellulose and lignocellulose fibres according to the invention can be used as such, in other words, they can be recovered, dried and mixed with some other matrix material, or fibre webs can be formed of a pulp containing these fibres without separating

and recovering the fibres. Electrically conductive fibres can be combined with different kinds of fibre products, such as papers, cardboards, fibreboards (e.g. MDF- and HDF-boards) and other compression products, like compression mouldings. These can also be used for the preparation of composite products, for example together with thermoplastics and cold-sets as well as combined with mineral fillers and building materials. According to the invention, it is thereby possible to produce e.g. building boards that can be identified by means of electrical measurements.

The electrically conductive polymer can be doped by means of organic doping agents without lowering the pH of the fibre dispersion below two. In this way, keratinization of fibre and reduction in durability of the sheet to be formed can be avoided. In addition, the organic acid, in particular the aromatic sulphonic acid, can be selected depending on the fibre to be treated such that the electrically conductive polymer can be bonded to the fibres.

In the following, the invention will be examined more closely with the aid of a detailed description and some working embodiments.

In the examples, there are references to the attached figures that include microscopic figures where a cross-section of a polyaniline treated fibre is presented, and when it can be seen from the figures how polyaniline has penetrated inside the fibre in the presence of different counter-ions.

Figures 1 and 2 depict the cross-section of a fibre treated with polyaniline doped with toluene sulphonic acid (TSA) presented as 200 fold enlargement (Figure 1) and as 500 fold enlargement, respectively.

Figures 3 and 4 show the corresponding micrographs of polyaniline doped with dodecylbenzene sulphonic acid (DBSA) and

Figures 5 and 6 show micrographs of polyaniline doped with hydrochloric acid (a counter example).

The fibre composition in accordance with the invention comprises a substrate composed of porous natural fibres, having electrically conductive polymers attached to this substrate. As stated above, the concentration of electrically conductive polymers should be sufficient so that the resistivity of the substrate (surface resistivity) can be reduced to a level of 10^{11}

ohm, preferably below that value and, most preferably, to a level of 10^8 ohm and if desired, even to a level of 10^4 ohm. Therefore, about 0.1 to 150 weight-% and preferably about 1 to 100 weight-% of polymer can be added with respect to the amount of the fibre.

Preferably, the amount of conductive polymer is from about 5 to 70 % and, most
5 preferably, from about 7.5 to 50 % of the gross weight of the fibre material.

According to the invention, polymers have been attached to the substrate composed of fibres in a way that they are not substantially out-washable. As a consequence to this, they do not end up e.g. in the short circulation water of a paper or a cardboard machine.

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Generally, it is assumed in the presented solution that the conductivity of fibres containing electrically conductive polymers can be substantially restored to the original level after wet cleaning, even if the counter-ion of the polymers would be washed out as a consequence of wet cleaning. Preferably, the conductivity of the electrically conductive polymers can be
15 restored to a level that is 3 decades weaker, at the most, than the original one (i.e. the surface resistivity is 3 decades greater). In order to restore the conductivity, the same counter-ion or some other substance can be used, as described in more details below.

Typically, about 20 w-% in maximum, preferably less than about 10 w-%, or even less
20 than 5 w-% of electrically conductive polymers are out-washed by water at $\text{pH } 7 \pm 0.3$ at a temperature of 25°C per one washing occasion. In wet cleaning, fibres are soaked and mixed in water at the pH and temperature conditions mentioned above and after about 10 minutes, water is removed and the fibres are separated and dried.

25 Depending on the doping agent and fixation conditions and because of the out-washing of the doping agent, the electrical conductivity (in terms of surface resistivity) can drop with a magnitude of 4 to 8 for each washing time, e.g. from value 10^4 to 10^8 Ohm after 6 washes by water.

30 The conductivity of the fibres can be determined by forming a uniform fibre layer of a fibre suspension and then, by sucking water off by vacuum filtration and by drying the fibre layer at a temperature of 50°C in maximum before the measurement (see Examples 7 and 8 below). The electrical conductivity can also be determined from a sheet prepared by a standard method (e.g. SCAN C26:76).

In order to get the conductive polymer attached to fibres so that it cannot be washed out, the fibres should be composed of porous natural fibres that are in a form of separate and loose fibres before a uniform fibre matrix is optionally formed of them. Precursors of the polymers, e.g. a salt formed by the monomer and the doping agent, are at first allowed to penetrate fibre pores (into the interior of fibres) and then, a polymerization reaction is carried out, whereby attachment of the polymers to these fibres is achieved both on top of the fibres and inside them. When separate and loose fibres are used to form a fibre matrix, for example, by a paper or a cardboard machine and when this matrix comprises a uniform fibre layer, e.g., in a form of paper or cardboard, this results in a situation where an electrically conductive polymer has penetrated the fibres and a majority of the polymer is located inside the fibre matrix. As a consequence, the polymer is homogeneously dispersed in the fibre layer. By homogeneous dispersion we mean that the surface resistivity of paper or cardboard as a function of location varies about 10 % in maximum, preferably about 5 % in maximum.

The weight per square of a web that forms the fibre matrix is generally about 5 to 700 g/m², typically about 20 to 500 g/m² and, for example, about 30 to 150 g/m² for paper and 80 to 300 g/m² for cardboard.

The porous fibres used in the invention are cellulose fibres, lignocellulose fibres, cellulose fibres of cereal crops, pentosan of cereals, cotton lint, Abaca hemp fibres, sisal fibres, ramie fibres, flax fibres, reed canary grass fibres or bastose. It is most preferable to use cellulose or lignocellulose pulp made by defibrating annual or perennial plants, such as chemical or mechanical pulp or mechano-chemical pulp. The following can be mentioned of chemical pulping methods: sulphate pulping, continued sulphate pulping, sulphite pulping, polysulphide pulping, organosolv-pulpings (e.g. Milox-pulping) and soda pulping. The most important ones of mechanical pulping methods are grinding (GW), pressure grinding (PGW), thermomechanical pulping (TMP) and refining (RMP) and the most important ones of mechano-chemical methods are CTMP and CMP methods. The pulp can be bleached or unbleached.

It is characteristic to the porous fibres to be used that they are able to absorb at least an amount of water corresponding their own weight (before a polymer and/or a precursor of it

are/is impregnated to them). Most suitably, the fibres to be used are capable of absorbing an amount of water, which is from 1.5 to 20 times their weight. Generally, the size of fibres is from about 0.01 to 10 mm. Depending on the desired dewatering efficiency, the fibres are generally post-beaten to a drainability that is from 80 to 650 ml CSF, preferably
5 from about 120 to 560 ml CSF. The fibres are "separate and loose" which means that they can be processed dry in a fluff state. In comparison with known solutions where a polymer is attached to cloths, a considerably better homogeneity is reached with the invention.

In the present invention, "Electrically conductive polymer" or "Conductive polymer"
10 means inherently conductive polymers (ICP), which are "doped" (furnished, processed) in order to generate charge carriers (holes and electrons). Common to all electrically conductive polymers are the conjugated double bonds of the backbone chain (alternate single and double bonds, delocalized silicon electron system), which enable the movement of the charge carriers. Electrically conductive polymers have both ionic and electronic
15 conductivity, which can be utilized in various applications. The conductivity of electrically conductive polymers can fluctuate and be regulated within the whole conductivity range, from an insulating material to a metallic conductor. Generally, a polymer is considered to be electrically conductive if its maximum resistance is 10^{11} ohm (as surface resistance).

20 An electrically conductive polymer can be bound in fibres both in an electrically conductive and in an electrically non-conductive form. Consequently, the term "electrically conductive polymer" in the claims presented below also means a polymer that is non-conductive at the time of reference, but which, however, can be brought to an electrically conductive state, for instance by using a suitable doping agent treatment.

25 Polyaniline, polypyrrole, polyacetylene, polyparaphenyl or polythiophene, or derivatives or mixtures of them are used as electrically conductive polymers. Among the derivatives, especially the alkyl and aryl derivatives and the chlorine and bromine-substituted derivatives of the polymers mentioned above, are worth mentioning. If needed, electrically
30 conductive particles, such as graphite or carbon black can be added, too.

Polyaniline is particularly preferred in the present invention. The monomer in the aniline polymer is aniline or its derivative, the nitrogen atom of which is in most cases bonded to the para-position carbon of the benzene ring of the next unit. The unsubstituted polyaniline

can be in different forms, among which the emeraldine form, which is characterized by a clear, emerald-green colour, which stands for its name, is generally used for conductive polymer applications

- 5 By doping, the electrically neutral polyaniline can be converted into a conductive polyaniline-complex. The doping agents used in the present invention can vary widely and they are generally employed when doping conjugated polymers into an electrically conductive or semiconductive form.
- 10 Protonic acids are known doping agents in the field of inherent conductive polymers, as will appear from the references by J.-C. Chiang and Alan G. MacDiarmid and in the W. R. Salaneck citation:
 - o Chiang et al., Synth. Metals (1986) 13:193-205
 - o MacDiarmid et al., Papers from the 6th European Physical Society Industrial
 - 15 Workshop Eur. Phys. Soc.
 - o Salaneck et al., Synth. Metals (1986) 13:291-297 No Month Available.

Such doping agents comprise organic acids, and their derivatives, among which sulphonic acids, picric acid, n-nitrobenzene acid, dichloric acetic acid and polymer acids are typical
20 examples. If desired, more than one doping acid can be used.

Preferably, a functional acid is used for doping, such as sulphonic acid, particularly aromatic sulphonic acid, which comprises one aromatic ring, or two merged rings, in which case at least one ring may have a polar or a non-polar cyclic substituent, such as a
25 functional group (for instance a hydroxyl group) or a hydrocarbon chain, such as an alkyl chain with 1-20 carbons. Examples of these are alkyl-benzene sulphonic acids and dialkylbenzene sulphonic acids (where the alkyl comprises 1-20 carbon atoms), other branched benzene sulphonic acids, aromatic diesters of phosphoric acid, etc.

30 The following can be particularly mentioned:

MSAs (methylsulphonic acids),

Ethylsulphonic acids

BSAs (benzoic sulphonic acids)

TSAs (toluene sulphonic acids)

DBSAs (dodecylbenzene sulphonic acids)

Ethylbenzene sulphonic acids

PSAs (phenol sulphonic acids or hydroxybenzene sulphonic acids)

5 CSAs (camphor sulphonic acids)

AMPSA (2-acrylamide-1-propanesulphonic acid)

Vinylsulphonic acids

Isophthalic sulphonic acid and esters

PPA (phenyl phosphine acids)

10 Phosphone acetic acid,

DIOHP (bis(2-ethyl hexyl hydrogenphosphate))

Chlorobenzene sulphonic acids

Pyridine sulphonic acids

Anisidine sulphonic acids

15 Aniline sulphonic acids

Quinoline sulphonic acids

Naphthalene sulphonic acids

Sulphosalicylic acids

Phosphonic acids

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Polymers which are functionalized at their ends by sulphonic acid [polystyrene (PSSA), polyolefins, polyethylene oxide, polyvinyls], as well as sulphonated polyparaphenylenes and sulphonated aromatic polyamides and alike substances, can be mentioned as examples of polymeric acids.

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Preferred acids are dodecylbenzene sulphonic acid (DBSA), camphor sulphonic acid, para-toluene sulphonic acid and phenol sulphonic acid.

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The preparation of polyaniline complexes has been described in great detail in, e.g., EP Published Patent Applications Nos. 545 729 and 582 919 and in FI Patent Applications Nos. 932557, 932578 and 940626, the contents of which are herewith incorporated by reference.

According to a preferred embodiment of the invention, the doping agent of an electrically conductive polymer is selected so that a salt formed by a parent substance (monomer) of an electrically conductive polymer and the doping agent is soluble in the medium, such as water, used for attachment of the polymer. In particular, this concerns a case where an
5 electrically conductive polymer is attached to fibres that have been produced by chemical pulping.

Doping agents with surface activity and/or hydrophobic characteristics can be used when the fibre to be treated includes lignin even though the salt formed by them and the parent
10 substance of an electrically conductive polymer is slightly soluble in the intermediate agent. Fibres like these are lignocellulose fibres obtained from mechanical pulping. Dodecylbenzene sulphonic acid (DBSA) can be mentioned as an example of the doping agents.

15 Oxidizing agents are generally used in polymerization of a monomeric compound into a corresponding electrically conductive polymer. Preferred oxidizing agents are polyatomic metallic salts such as iron(III) salts and per-compounds like peroxides, peracids, persulphates, perborates, permanganates, perchlorates and chlorates, nitrates and quinones. The amount of an oxidizing agent in relation to the monomer is generally from 10:1 to 1:1,
20 most preferably from about 5:1 to 2:1 (parts by weight) or from 4:1 to 1:1 as mole fractions (oxidative/monomer).

Polyaniline can be attached to the fibres both in electrically conductive and non-conductive form. Polyaniline has to be doped by a counter-ion for converting it into a conductive
25 form. It is particularly preferred to attach polyaniline to fibres in an electrically conductive form because it can be assumed that the binding of polyaniline happens, at least partially, with the aid of the doping agent as will be described in more details below.

The electrical resistivity of the fibre composition built up in accordance with the invention,
30 is generally about $50 - 10^8$ ohm.

The product can be produced by bringing porous fibres in intimate contact with a monomer that forms an electrically conductive polymer, in a suitable medium, in particular in an aqueous medium. Organic, polar and nonpolar solvents can be used in addition to water

and aqueous solutions. By "intimate contact" it is meant that a fine pulp that includes fibres and a monomeric precursor of polymer and/or a doping agent of polymer is mixed vigorously to have the monomer and/or doping agent efficiently distributed in the fibre material. Thus, "aqueous medium" stands for both water and water solutions in which fibres are slurried. Typically, the consistency of the aqueous slurry is from 0.1 to 50 % (weight/weight), preferably from about 0.5 to 30 %, and particularly from about 0.7 to 20 %. Thereafter, the counter-ion or the monomer of the electrically conductive agent to be polymerized, respectively, can be dissolved in the aqueous phase. The amount of the doping agent varies depending on the amount of a monomer. Generally, the amount of monomer is from about 0.1 to 200 % of the amount of fibre, typically about 1 to 150 w-%, preferably about 5 to 120 w-%, and particularly about 10 to 100 w-%. Generally, the amount of a counter-ion can be equimolar with the amount of monomer but it can also be approximately the amount of moles of the monomer ± 30 %.

The temperature is generally above 0 °C but below room temperature. Typically, the temperature is from about 1 to 18 °C, preferably from about 2 to 15 °C.

Generally, an acidic counter-ion is used and the pH of the aqueous phase, used in pairing of fibres and a polymer/monomer, is most suitably clearly acidic, preferably the pH is below 5, and most preferably above 2. Too low pH values can affect disadvantageously the mechanical properties of the fibres and this is why the preferred pH environment is from about 2 to 5 and, most suitably, from 2 to 3.

As stated above, in accordance with the invention, an aggregate (a complex or a salt) formed by the monomer and the doping agent is first introduced among fibres and, thereafter, the monomer is polymerized in order to attach the polymer to the fibres in such a way that it is not washed out at the demanding conditions of paper making. The affinity of the porous fibres and of an electrically conductive polymer, respectively, for mutual bonding can be improved by considering the following features:

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- a) The type of a counter-ion
- b) The solubility of the salt formed by a monomer and a counter-ion
- c) The concentration of a monomer and a counter-ion, and
- d) The type of a fibre

The latter item has already been discussed above: In order to increase the affinity for mutual bonding between the porous fibres and the electrically conductive polymer, the polymerization reaction is carried out in an aqueous medium which contains porous fibres, to allow for the attachment of the polymer formed via polymerization to the porous fibres. Typically, the monomer to be polymerized into an electrically conductive polymer and the doping agent are first reacted with each other to form a salt or a complex in an aqueous solution and then, this is brought in contact with porous fibres, and allowed to penetrate the fibres. Thereafter, a monomer is polymerized in fibres, resulting in a polymer that is homogeneously dispersed throughout the pulp. The reaction of the monomer and the polymer catalyst can be performed in the presence of the fibres. The doping agent can even be added before the monomer, whereby it (i.e. the doping agent) is allowed to absorb into fibres before the monomer. By this solution, the attachment of the monomer and thereby, the attachment of the polymer to fibres, can further be improved.

When the doping agent is selected, it is an aim to reach a situation where the affinity towards mutual bonding of porous fibres and an electrically conductive polymer is as strong as possible. In the present invention, it has been found that the selection of the doping agent depends on the surface of the cellulose fibre. According to one preferred embodiment, the affinity of the porous fibres and an electrically conductive polymer towards mutual bonding is increased by selecting fibres whose surface is at least partially covered by lignin. This means thereby fibres of mechanical or mechanical-chemical pulp that have, for example, lignin from a laminate interlayer on their surface. It is known that lignin contains phenyl and phenol structures and hence, it has been observed that it is preferred to have a doping agent with aliphatic hydrocarbon structures that increase the hydrophobic nature of the doping agent. In experiments which we have carried out, we have found that polyaniline can be bonded to mechanical pulp fibres quite well by using dodecylbenzene sulphonic acid, or a similar compound, as a doping agent. "Similar compound" means a compound with alkyl or dialkyl side chain(s) with more than four and preferably, about 5 to 20 carbon atoms attached to an aromatic group. It would appear to be possible to increase bonding by arranging adjacent aliphatic hydrocarbon and aromatic hydrocarbon structures at the bonding surfaces.

In the examples presented below, an ordinary chemical pulp (bleached softwood cellulose cooked by the sulphate method) has also been used. In surfaces of this kind of pulp, there is a great deal of aliphatic anhydrohexose or anhydropentose chains, originating from cellulose or hemicellulose, and these chains have typical aliphatic character. In order to
5 improve bonding to these, it is advantageous to use a doping agent that is more hydrophilic than alkyl benzene sulphonic acid i.e. an agent that has at most a lower alkyl group as a substitute of an aromatic ring. Instead, the ring can contain functionalized groups that increase the hydrophilic nature of the substance. In accordance with this, para-toluene sulphonic acid and substances alike it are especially preferable of the doping agents
10 mentioned above. It seems that adjacent aliphatic structures and aromatic hydrocarbon structures, respectively, are formed in bonding sites of a doping agent and fibres, in this case too.

Electrically conductive cellulose and lignocellulose fibres, in accordance with the
15 invention, are advantageously used in the production of electrically conductive paper or cardboard products. Fibres can be recovered after production, dried and then used in a dry form in a desired application or reused as a suspension. After treatment in accordance with the invention, fibres can be further transferred to the manufacturing of paper or cardboard. The fibres are then carried forward most adequately in an aqueous pulp and they are mixed
20 with other fibres e.g. in the head box of a paper machine. It is essential that by mixing the fibres according to the invention with such conventional plant fibres that do not contain an electrically conductive polymer component, an electrically conductive fibre composition is obtained which contains an evenly dispersed electrically conductive component. In general, fibres in accordance with the invention, are added from about 1 to 50 weight -% of
25 dry substance of the fibre product, preferably from about 2 to 30 weight-%. A fibre matrix where an electrically conductive polymer is quite evenly distributed is obtained when producing a product by a paper or a cardboard machine.

Products to be produced can be employed in ESD applications or for forming security
30 marks.

The following examples illustrate the invention. They indicate more closely the details of the preferred embodiments of the invention.

SUMMARY OF THE EXAMPLES

In this work, aniline was polymerized in the presence of ground, coniferous cellulose fibre using different counter-ions. The objective of the work was primarily to attach polyaniline delivered by the polymerization on the surface of the fibre and thereafter, to produce electrically conductive paper of fibres absorbed with polyaniline.

The parent substances used in this work were water, aniline, dodecylbenzene sulphonic acid (A), p-toluene sulphonic acid (B), citric acid (C), ammonium persulfate (Degussa) and ground, softwood cellulosic pulp (TKK, Technical University of Helsinki). The work was carried out as an emulsion polymerization in a 5 l glass bulb that was cooled in an ice water bath so that the temperature of the exothermic reaction was maintained stable during the whole reaction. The polymerization was done in a same way with all three counter-ions.

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Hydrochloric acid was also used as a counter-ion, for comparison.

The pulp with consistence from 5 to 30 % was added in water so that 1 % mixture was formed regarding the fibre (e.g. 30 g of fibre in 3000 g of water). Then, counter-ion (A, B or C) was dissolved in this using the corresponding amount of moles than that for aniline. The addition of aniline from 10 to 100 w-% of the amount of the fibre (e.g. 3 g) was followed. Then, the mixture was cooled below temperature of 10 °C. APS-aqueous solution (7.4 %) was used as an oxidant and the amount corresponding 1.03 times the amount of aniline moles, was used for the APS. Thereafter, the oxidant was gradually added to the mixture within about 3 hours after what the temperature was allowed to rise to room temperature.

The pulp press water of the mixture comprised of polyaniline, chemical pulp fibre and water was then separated by centrifugation. The product was slurried in water once and centrifuged again when the residuals of APS-salts were washed away. Finished and washed product was sent to TKK for the production of paper sheets. The surface resistivities of the fibres filtrated on the top of filter paper and of those fibres, which were dried were the following:

PAN-DBSA 100 % of the amount of the fibre: 10×10^3 Ohm

PAN-DBSA 10 % of the amount of the fibre: 10×10^4 Ohm

PAN-TSA 10 % of the amount of the fibre: 10×10^7 Ohm

PAN-TSA 25 % of the amount of the fibre : 10×10^4 Ohm

5 PAN-TSA 50 % of the amount of the fibre: 10×10^3 Ohm

PAN-citric acid 10 % of the amount of the fibre: $10 \times 10^5 \dots 11$ Ohm

(PAN = polyaniline)

10 The enclosed micrographs show a cross section of PAN-treated fibre i.e. how PAN has penetrated into the fibre in the presence of different counter-ions. Figures 1, 3 and 5 are 200- fold enlargements with toluene sulphonic acid (TSA) and dodecylbenzene sulphonic acid (DBSA) as counter-ions and HCl as a counter example. Figures 2, 4 and 6 are 500- fold enlargements, respectively.

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On the ground of the figures it seems as follows: DBSA forms a water insoluble salt with aniline when PAN stays on the surface and partly as particles between fibres. TSA impregnates very well into the fibre structure as a soluble aniline salt. HCl forms a soluble salt too but PAN stays as a clear layer on the surface of the fibre. In fact inside the fibre, 20 i.e. in the lumen, hardly any PAN can be seen with any counter-ion. Hence, it can be stated that besides a mineral acid, alike with strong hydrochloric acid, keratinizes fibres, it leaves polyaniline on the surface of the fibre when an organic doping agent enables the polymerization of polyaniline into the interior of the fibre. As a result, polyaniline stays better in the fibre even when mechanical erosion is directed to them.

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Surface resistivities measured at VTT were measured by an apparatus which measures electrical resistance between two parallel, metallic rods of 6.5 cm length each and these rods being placed on the surface of the sample. The rods are at 4 cm distance from each other. The measurement voltage at the conductive area is 10 V in the area of less than 30 10×10^5 Ohm and 100 V in the area of more than 10×10^5 Ohm.

As mechanisms of retention between a counter-ion and a fibre and mechanisms leading to that were still unclear at this status, more polymerizations were carried out both to the chemical pulp fibre and lignin fibres TMP-reject, and TMP/GW-fibre. These

polymerizations were done in a corresponding way than the previous ones except that phenol sulphonic acid (PSA), camphor sulphonic acid (CSA) and methan sulphonic acid (MSA) were used as counter-ions. Products were washed by filtration and elutriating them to water again. In connection to the filtration, a filter cake was prepared directly from the reaction mixture and after the third and the sixth wash. The product was washed until pH had risen above value 6. Surface resistivities were measured from dry filter cakes and samples taken from pulps were analysed for the attachment of the polymer to the fibre in KCl by a light microscope. The microscopic figures are presented in appendix II. A summary of treatings done with different counter-ions and fibres has been presented in Table I.

TABLE I. Polymerization of aniline with different counter-ions in the presence of woodfree and ligneous fibres.

<u>Ligneous fibre: TMP-reject or TMP/GW-fibre</u>					
	<u>DBSA</u> Tmp	<u>TSA</u> Tmp	<u>PSA</u> Tmp (tmp/gw)	<u>CSA</u> Tmp	<u>MSA</u> Tmp/gw
Aniline salt	<u>Solid</u>	Water soluble	Water soluble	Water soluble	Water soluble
Colour reaction to green	2 - 4 h	> 12 h	10 min -> 1 h (10 - 50 min)	4 - 6 h	3 - 8 h
Concentration of aniline	0.25 %	0.08%	0.17% (0.25%)	0.18 %	0.5 %
Initial pH			2	2	2.57
Washes -> pH 6	9	8	6	6	7
Initial resistivity of cake, Ω	10exp4	10exp4	10exp4 (10exp3)	10exp5	10exp3
Resistivity 3 washes, Ω	10exp4		10exp5...6 (10exp4)	10exp7	10exp5
Resistivity 6 washes, Ω	10exp5	10exp8	10exp7 (10exp5...6)	10exp12	10exp6...7
Attached to fibre*	2...3	2	2 (1)	2	2
<u>Chemical pulp fibre</u>					
Colour reaction to green	3 h	4 h	3 h	4 h	6 h
Concentration of aniline	0.13 %	0.32 %	0.25 %	0.25 %	0.25 %
Initial pH		1.66	1.83	1.71	2.9
Washes -> pH 6	5	12	10	8	7
Initial resistivity of cake, Ω	10exp4... 5	10exp4	10exp4	10exp4	10exp4
Resistivity 3 washes, Ω		10exp4	10exp5	10exp6	10exp6
Resistivity 6 washes, Ω	10exp12	10exp5	10exp7	10exp7	10exp9
Attached to fibre*	3...4	1	1	1	1

* The attachment to the fibre has been evaluated by using a microscopic scale: 1 = inside the fibre, 2 = partially in the fibre, 3 = attached on the surface, 4 = polymer loose and between

In addition to reactions presented in Table I, reactions where sulphuric acid was used as a counter-ion were carried out. Reactions by using two different aniline-counter-ion concentrations were performed when a reaction both with water insoluble and soluble aniline salt was achieved.

TABLE II. Polymerization of aniline using sulphuric acid (H_2SO_4) as a counter-ion in the presence of fibre in the reaction mixture.

	TMP/GW-fibre	Chemical pulp fibre	Chemical pulp fibre
Aniline salt	Water soluble	Water soluble	Solid
Colour reaction to green	2 h yellow -> green	1.5 h blue -> green	10 minutes
Aniline concentration	0.25 %	0.25 %	13 %
Initial pH	2.85	2.88	2.08
Washes -> pH 6	9	9	17
Initial resistivity of cake, Ω	10exp4	10exp4	10exp3
Resistivity 3 washes, Ω	10exp5	10exp5	10exp3
Resistivity 6 washes, Ω	10exp7	10exp7	10exp4
Attached to fibre *	2 and 4	1	1 and 3, Inside and on surface

* The attachment to the fibre has been evaluated by using a microscopic scale: 1 = inside the fibre, 2 = partially in the fibre, 3 = attached on the surface, 4 = polymer loose and between

Reactions in accordance with Table II showed that the solubility of salt could depend on the concentration of salt too. The purpose of experiments was to demonstrate that a water insoluble aniline-counter-ion salt does not attach to the fibre as well as a soluble salt. The demonstration of this, however, was a failure because the amount of the insoluble salt in comparison with the chemical pulp fibre to be treated was more than ten-fold. In other reactions, a maximum of 25 % of aniline was used out of the amount of fibre. This resulted in a situation where there was so much polyaniline present that washing it out of the fibre was complicated. In addition, the high concentration of sulphuric acid may have changed the structure of the fibre before aniline became polymerized.

In the attached examples of Table I only DBSA aniline salt is water insoluble, also at low concentrations. Due to its solid state and large molecule structure and surface-active nature of dodecyl benzene sulphonic acid (DBSA), the penetration of polyaniline into the chemical pulp fibre was weak. Ligneous fibre, in its turn, includes also multiple different kinds of active groups to which the attachment is easier, even for long chain DBSA.

Concerning water-soluble aniline counter-ions, the attachment to a fibre and impregnation to the fibre with water has been easier. In addition, the impregnation to a chemical pulp fibre is easier than that to a ligneous fibre because of the chemical and physical nature of lignin.

Purely when mixing polyaniline with fibre (Example 13, where 25 % of polyaniline of the amount of the fibre has been mixed with the chemical pulp fibre) polyaniline does not get properly impregnated into the fibre. Hence, polyaniline is remarkably easier to be washed out of the fibre mixture than of a mixture where polyaniline has been prepared in the presence of the fibre.

The conductivity of an electrically conductive fibre product can be affected by the type of a fibre (cellulosic pulp or ligneous), the selection of a counter-ion (water-soluble/solid, size and form of a counter-ion), the amount of aniline-counter-ion salt in relation to the amount of fibre and, in case of slightly soluble salt, by the concentration of a salt in a reaction mixture. In after-treatment, effects can be reached primarily by the amount of the used washing water and the number of washing occasions when part of counter-ions is washed out with water resulting in dedoping of a product.

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PREPARATION EXAMPLES

EXAMPLE 1. In presence of chemical pulp fibre, polymerization of aniline where dodecyl benzene sulphonic acid was used as a counter-ion. The amount of aniline is equal to the amount of fibre.

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A total of 1500 ml of water was put in a flask and then, 52.5 g of dodecyl benzene sulphonic acid was added. Then, dodecyl benzene sulphonic acid was allowed to solve in water and thereafter, 1015 g of woodfree pulp was added. The woodfree pulp contained 15

g of coniferous chemical pulp fibre per 1000 g of water. After fifteen minutes, 15 g of aniline was added. Aniline and dodecyl benzene sulphonic acid form water insoluble salt that was allowed to mix for 30 minutes. The mixture was cooled in an icewater bath to the temperature of 12°C. Then, 36.8 g of ammonium persulphate was dissolved in 200 ml of water and this solution was added into the mixture during 3 hours. After addition of ammonium persulphate, blending was continued for 2.5 hours and this resulted in a very dark green, almost black chemical pulp fibre-polyaniline suspension in water. Reaction water was washed away from the product by centrifugation and it was elutriated in water again to a suspension that had about 7.4 % of dry substance. The surface resistivity of the chemical pulp fibre that contained about 100 % of polyaniline in relation to the fibre, was 10×10^3 Ohm. The product was delivered to TKK to be tested in paper production.

EXAMPLE 2. In presence of chemical pulp fibre, polymerization of aniline where dodecyl benzene sulphonic acid was used as a counter-ion. The amount of aniline was 10 % of the amount of fibre.

A total of 400 ml of water was put in a flask and then, 5.25 g of dodecyl benzene sulphonic acid was added. Then, dodecyl benzene sulphonic acid was allowed to solve in water and thereafter, 1.5 g of aniline was added in mixture. Aniline and dodecyl benzene sulphonic acid form a water insoluble salt that was allowed to mix for 15 minutes. A total of 983.3 g of cold dispersed chemical pine pulp, with pH 5.5, was added into the mixture. The woodfree pulp contained 15 g of fibre per one litre of pulp. The mixture was cooled in an icewater bath to the temperature of 8°C. Then, 3.7 g of ammonium persulphate was dissolved in 50 ml of water and this solution was added into the mixture during 1.5 hours. After addition of ammonium persulphate, blending was continued for 5 hours and this resulted in a very dark green, almost black chemical pulp fibre-polyaniline suspension in water. Reaction water was washed away from the product by centrifugation and it was elutriated in water again to a suspension that had about 1.6 % of dry substance. The surface resistivity of the chemical pulp fibre that was washed once and contained about 10 % of polyaniline, was 10×10^4 Ohm. The product was delivered to TKK to be tested in paper production.

EXAMPLE 3. In presence of chemical pulp fibre, polymerization of aniline where dodecyl benzene sulphonic acid was used as a counter-ion. The amount of aniline was 10 % of the amount of fibre. Fibre added before the counter-ion.

5 A total of 500 g of water was put in a flask and then, 1000 g of cold dispersed chemical pine pulp was added. The pulp included 15 g of fibre per 1000 g of pulp. Then, 5.3 g of dodecyl benzene sulphonic acid was added which was allowed to dissolve for 10 minutes. Thereafter, 1.5 g of aniline was added when a water insoluble, white aniline-dodecyl benzene sulphonic acid salt was formed. The mixture was cooled in an icewater bath to the
10 temperature of 8°C. Then, 3.7 g of ammonium persulphate was dissolved in 50 ml of water and this solution was added into the mixture during 1.5 hours. After addition of ammonium persulphate, blending was continued for 4 hours and this resulted in a very dark green, almost black chemical pulp fibre-polyaniline suspension in water. Reaction water was washed away from the product by centrifugation and it was elutriated in water again to a
15 suspension that had about 1.6 % of dry substance. The surface resistivity of the chemical pulp fibre that was washed once and contained about 10 % of polyaniline, was 10×10^4 Ohm.

EXAMPLE 4. In presence of chemical pulp fibre, polymerization of aniline where
20 dodecyl benzene sulphonic acid was used as a counter-ion. The amount of aniline was 10 % of the amount of fibre. More dilute reaction mixture.

A total of 2780 g of water was put in a flask and then, 300 g of cold dispersed chemical pine pulp was added. The pulp included 10 g of fibre per 100 g of pulp. Then, 10.5 g of
25 dodecyl benzene sulphonic acid was added which was allowed to dissolve for 20 minutes. Thereafter, 3 g of aniline was added when a water insoluble, white aniline-dodecyl benzene sulphonic acid salt was formed. The mixture was cooled during blending in an icewater bath to the temperature of 11°C. Then, 7.4 g of ammonium persulphate was dissolved in 100 ml of water and this solution was added into the mixture during 2.5 hours.
30 After addition of ammonium persulphate, blending was continued for 5 hours and this resulted in a very dark green, almost black chemical pulp fibre-polyaniline suspension in water. Reaction water was washed away from the product by centrifugation and it was elutriated in water again to a suspension that had about 2.3 % of dry substance. Paper

sheets that contained different amounts of treated cellulosic pulp were prepared of chemical pulp fibre including 10 % of polyaniline, at TKK.

EXAMPLE 5. In presence of chemical pulp fibre, polymerization of aniline where p-toluene sulphonic acid was used as a counter-ion. The amount of aniline was 10 % of the amount of fibre.

A total of 1970 g of water was put in a flask and then, 295 g of cold dispersed pine woodfree pulp was added. The pulp included 10 g of fibre per 100 g of pulp. Then, 6.13 g of p-toluene sulphonic acid was added which was allowed to dissolve for 50 minutes. Thereafter, 3 g of aniline was added when a water-soluble aniline-p-toluene sulphonic acid salt was formed and the mixture became a bit brownish. The mixture was cooled during blending in an ice-water bath to the temperature of 9°C. Then, 7.4 g of ammonium persulphate was dissolved in 100 ml of water and this solution was added into the mixture during one hour. After addition of ammonium persulphate, blending was continued for 5 hours and it was left stand overnight. This resulted in almost black, a bit greenish chemical pulp fibre-polyaniline suspension in water. Reaction water was washed away from the product by centrifugation. The product was washed by filtration once and it was elutriated in water again to a suspension that had about 7.1 % of dry substance. The surface resistivity of the sheet prepared by filtration of chemical pulp fibre, containing about 10 % of polyaniline, was 10×10^7 Ohm. Paper sheets that contained different amounts of treated cellulosic pulp were prepared of the product, at TKK.

EXAMPLE 6. In presence of chemical pulp fibre, polymerization of aniline where citric acid was used as a counter-ion. The amount of aniline was 10 % of the amount of fibre.

A total of 1970 g of water was put in a flask and then, 294.8 g of cold dispersed pine woodfree pulp was added. The pulp included 10 g of fibre per 100 g of pulp. Then, 6.19 g of citric acid was added which was allowed to dissolve for 40 minutes. Thereafter, 3 g of aniline was added when a water-soluble aniline-citric acid salt was formed. The mixture was cooled during blending in an ice-water bath to the temperature of 9°C. Then, 7.4 g of ammonium persulphate was dissolved in water (100 ml) and this solution was added into the mixture during 1.5 hour. After addition of ammonium persulphate, blending was continued for 6 hours resulting in brown product. After leaving the mixture stand

overnight, a black chemical pulp fibre-polyaniline suspension in water was obtained. Reaction water was washed away from the product by filtration. The product was elutriated in water again to a suspension that had about 6.1 % of dry substance. The surface resistivity of the sheet prepared by filtration of chemical pulp fibre containing about 10 % of polyaniline, was 10×10^5 Ohm. Paper sheets that contained different amounts of treated cellulosic pulp were prepared of the product, at TKK.

EXAMPLE 7. In presence of chemical pulp fibre, polymerization of aniline where p-toluene sulphonic acid was used as a counter-ion. The amount of aniline was 25 % of the amount of fibre.

A total of 1700 g of water was put in a flask and then, 300 g of cold dispersed pine woodfree pulp was added. The pulp included 10 g of fibre per 100 g of pulp. Then, 15.3 g of p-toluene sulphonic acid was added which was allowed to dissolve for 15 minutes. Thereafter, 0.02 g of phenyldiamine was added followed by mixing for 15 minutes and then, 7.5 g of aniline was added. A water-soluble aniline-p-toluene sulphonic acid salt is formed and the mixture becomes a bit brownish. . The mixture was cooled during blending in an ice-water bath to the temperature of 9°C. Then, ammonium persulphate (18,5 g) was dissolved in 200 ml of water and this solution was added into the mixture during one hour. After addition of ammonium persulphate, blending was continued for 3 hours and then, left stand overnight, resulting in almost black, a bit greenish, chemical pulp fibre-polyaniline suspension in water. Reaction water was washed away from the product by centrifugation. The product was washed once by filtration when the pH of washing water was 2.0. The product was elutriated in water again to a suspension that had 5.5 % of dry substance. The surface resistivity of the sheet prepared by filtration of chemical pulp fibre, containing about 25 % of polyaniline, is 10×10^4 Ohm. Paper sheets that contained different amounts of treated cellulosic pulp were prepared of the product, at TKK.

ESIMERKKI 8. In presence of chemical pulp fibre, polymerization of aniline where p-toluene sulphonic acid was used as a counter-ion. The amount of aniline was 50 % of the amount of fibre.

A total of 1700 g of water was put in a flask and then, 300 g of cold dispersed pine woodfree pulp was added. The pulp included 10 g of fibre per 100 g of pulp. Then, 30.6 g

of p-toluene sulphonic acid was added which was allowed to dissolve for 15 minutes. Thereafter, 0.04 g of phenyldiamine was added followed by mixing for 15 minutes and then, 15 g of aniline was added. A water-soluble aniline-p-toluene sulphonic acid salt was formed and the mixture becomes a bit brownish. . The mixture was cooled during blending
 5 in an ice-water bath to the temperature of 9°C. Then, ammonium persulphate (37 g) was dissolved in 400 ml of water and this solution was added into the mixture during two hours. After addition of ammonium persulphate, blending was continued for 2 hours and then, left stand overnight resulting in almost black, slightly greenish, chemical pulp fibre-polyaniline suspension in water. Reaction water (pH = 1.3) was washed away from the
 10 product by centrifugation. The product was washed once by filtration when the pH of washing water was 1.7. The product was elutriated in water again to a suspension that had 7.0 % of dry substance. The surface resistivity of the sheet prepared by filtration of chemical pulp fibre, containing about 50 % of polyaniline, is 10×10^3 Ohm. Paper sheets that contained different amounts of treated cellulosic pulp were prepared of the product, at
 15 TKK.

EXAMPLE 9. In presence of chemical pulp fibre, polymerization of aniline where p-toluene sulphonic acid was used as a counter-ion. The amount of aniline was 25 % of the amount of fibre.

20 A total of 2400 g of ligneous fibre pulp (TMP reject) that included 4.27 g of fibre per one litre of water i.e., a total of 20 g of fibre, was put in a flask. Then, 10.2 g of p-toluene sulphonic acid was added which was allowed to dissolve for 25 minutes. Thereafter, 5 g of aniline was added. A water-soluble aniline-p-toluene sulphonic acid salt was formed and
 25 the mixture became yellow bright. The mixture was cooled during blending in an ice-water bath to the temperature of 9°C. Then, 14.7 g of ammonium persulphate was dissolved in 150 ml of water and this solution was added into the mixture during 3.5 hours. After addition of ammonium persulphate, blending was continued for 2 hours and then, the mixture was left stand overnight. At this phase, there were blond fibres in brown solution
 30 in the product. The product was left stand in cold store when it reacted to almost black, slightly greenish mixture little by little within about one week. Reaction water was washed away from the product by centrifugation. The product was washed once by water (pH of washing water was 2.2) and a sheet with surface resistance of 10×10^4 Ohm was prepared from part of the product through filtration. In addition to this, the product was washed

eight times to see how polyaniline detaches from the surface of the fibre. The pH of the eighth washing water was 6.34 and surface resistivity of the sheet prepared of it by filtration, was 10×10^9 Ohm. Microscopic figures have been taken of the treated fibres after the first and after the eighth wash.

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EXAMPLE 10. In presence of chemical pulp fibre, polymerization of aniline where p-toluene sulphonic acid was used as a counter-ion. The amount of aniline was 25 % of the amount of fibre.

10 A total of 200 g of cold dispersed ligneous woodfree pulp that included 20 g of pine fibre was put in a flask. Then, 1400 g of water was added in the pulp. A total of 10.21 g of p-toluene sulphonic acid was added in the mixture and it was allowed to dissolve for 15 minutes. Thereafter, 5 g of aniline was added when a water-soluble aniline-p-toluene sulphonic acid salt was formed. The mixture was cooled during blending in an ice-water
15 bath to the temperature of 10°C. Then, 12.9 g of ammonium persulphate was dissolved in 120 ml of water and this solution was added into the mixture during 1 hour and 15 minutes. After addition of ammonium persulphate, blending was continued for 3.5 hours and then, the mixture was left stand overnight. This resulted in a black, slightly greenish reaction mixture. Reaction water was washed away from the product by centrifugation. The product
20 was washed once by water (pH of washing water was 1.8) and a sheet with surface resistance of 10×10^4 Ohm was prepared from part of fibres through filtration. In addition to this, the product was washed 10 times to see how polyaniline detaches from the surface of the fibre. The pH of the tenth washing water was 5.0 and the surface resistivity of the sheet prepared from the corresponding fibre by filtration, was 10×10^6 Ohm. After this, the
25 fibres were dedoped by adding 2 % ammonia solution and by letting the fibres stand there overnight. The ammonia solution was filtrated away and the fibres were washed by water once when a sheet made from fibres through filtration did not conduct electricity. A total of 30 ml of 0.2 M H_2SO_4 was added in the residual pulp (about 10 g) and this was let to affect overnight. Surface resistivity of the sheet made of newly doped fibre by filtration
30 was 10×10^5 Ohm. Microscopic figures have been taken of the treated fibres, both of the dedoped and redoped ones, after the first and after the tenth wash.

EXAMPLE 11. In presence of chemical pulp fibre, polymerization of aniline where dodecyl benzene sulphonic acid was used as a counter-ion. The amount of aniline was 20 % of the amount of fibre.

- 5 A total of 100 g of cold dispersed chemical pulp that included 10 g of fibre, was put in a flask. Then, 7.0 g of dodecyl benzene sulphonic acid was added and was allowed to dissolve for one hour. Thereafter, 2.0 g of aniline was added when a water insoluble, white aniline-dodecyl benzene sulphonic acid salt was formed. The mixture was cooled during blending in an ice-water bath to the temperature of 7°C. Then, 5.15 g of ammonium
- 10 persulphate was dissolved in 60 ml of water and this solution was added into the mixture during 0.5 hours and thereafter, the product was very pale blue. After addition of ammonium persulphate, blending was continued for 5 hours during which the reaction had reached its end and the product was very dark green. The reaction mixture was still left stand overnight. Reaction water was washed away from the product by centrifugation. The
- 15 product was washed once by water and a sheet with surface resistance of $10 \times 10^4 \dots 5 \text{ Ohm}$ was prepared from part of it, through filtration. In addition to this, the product was washed five times to see how polyaniline detaches from the surface of the fibre. The pH of the fifth washing water was 6.2 and the surface resistivity of the sheet filtrated of it was $10 \times 10^{12} \text{ Ohm}$. After this, the fibres were still dedoped by 2 % ammonia solution,
- 20 overnight. Microscopic figures have been taken of the treated fibres, after the first and after the fifth wash and after the dedoping.

- EXAMPLE 12.** In presence of ligneous chemical pulp fibre, polymerization of aniline where dodecyl benzene sulphonic acid was used as a counter-ion. The amount of aniline
- 25 was 20 % of the amount of fibre.

- A total of 2000 g of ligneous fibre pulp (TMP reject) that included 10 g of fibre per one litre of water i.e., a total of 20 g of fibre, was put in a flask. Then, 17.5 g of dodecyl benzene sulphonic acid was added which was allowed to dissolve overnight (15 h).
- 30 Thereafter, 5 g of aniline was added when a water insoluble aniline-dodecyl benzene sulphonic acid salt was formed and the mixture became yellow bright. The mixture was cooled during blending in an ice-water bath to the temperature of 7 °C. Then, 14.1 g of ammonium persulphate was dissolved in 150 ml of water and this solution was added into the mixture during one hour. After addition of ammonium persulphate, blending was

continued for 5 hours after which the reaction mixture was dark green. The reaction mixture was let to stand overnight. Reaction water was washed away from the product by centrifugation. The product was washed three times by water and a sheet with surface resistance of 10×10^4 Ohm was prepared from part of the product through filtration. The surface resistivity was 10×10^4 Ohm \cdot m still after the fifth wash. The product was washed nine times to see how polyaniline detaches from the surface of the fibre. The pH of the ninth washing water was 6.24 and the surface resistivity of the sheet prepared of it by filtration was 10×10^{11} Ohm. Microscopic figures have been taken of the treated fibres after the fifth and after the ninth wash.

EXAMPLE 13. Mixture of polyaniline paste and chemical pulp fibre.

A total of 100 g of cold dispersed chemical pulp that included 10 g of fibre per one litre of water i.e., a total of 10 g of fibre, was put in a flask. Then, 1250 g of water together with 30.5 g of polyaniline that was polymerated by p-toluene sulphonic acid, and which had 8.2 % of dry substance, were added. The mixture was blended for 24 hours. Thereafter, water with pH 3.3 was filtrated away and a sheet with surface resistance of $10 \times 10^{7 \dots 8}$ Ohm was prepared from part of the product through filtration. The residual pulp was washed five times altogether. The pH of the fifth washing water was 6.4 and the surface resistivity of the sheet prepared of it by filtration, was 10×10^{12} Ohm. After the first and the fifth wash, microscopic figures have been taken where attachment of polyaniline on the surface of the fibre can be seen.

EXAMPLE 14. In presence of ligneous chemical pulp fibre, polymerization of aniline where p-toluene sulphonic acid was used as a counter-ion. The amount of aniline was 25 % of the amount of fibres. Fibre added after the addition of aniline.

A total of 1000 g of water was put in a flask in which 7.66 g of p-toluene sulphonic acid was dissolved. Then, 3.75 g of aniline was added when a reddish solution was formed. A total of 1500 g ligneous chemical pulp was added in the solution that included 15 g of fibre and then, the mixture became yellow. The mixture was cooled during blending in an ice-water bath to the temperature of 11°C. Then, 9.1 g of ammonium persulphate was dissolved in 95 ml of water and this solution was added into the mixture during 50

minutes. After addition of ammonium persulphate, blending was continued for 5 hours. After this, there were blond fibres in brown solution in the product. The product was left stand overnight when it reacted very slowly into dark, slightly greenish mixture. The objective of the experiment was to see whether changing the sequence of adding reagents before adding an oxidant accelerates the polymerization reaction in the presence of ligneous cellulosic pulp. After the experiment, it can be stated that the reaction did not accelerate.

EXAMPLE 15. In presence of ligneous thermomechanical fibre, polymerization of aniline where phenol sulphonic acid is used as a counter-ion. The amount of aniline was 25 % of the amount of fibres.

A total of 2000 g of thermomechanical pulp (TMP/GW) that included 20 g of fibre was put in a flask. Then, 14.4 g of 65 % aqueous solution of phenol sulphonic acid and 0.02 g of phenylenediamine were added into pulp when the mixture became maize yellow. It was mixed for 30 minutes and then, 5 g of aniline was added when a water-soluble aniline-phenolsulphonic acid salt was formed and the reaction mixture became yellow bright. The mixture was cooled during blending in an ice-water bath to the temperature of 9°C. Then, 12.3 g of ammonium persulphate was dissolved in 120 ml of water and this solution was added into the mixture during 40 minutes. After addition of ammonium persulphate, blending was continued for 5 hours. At this stage, the product was black and a bit greenish which means that the reaction had ended. The product was left stand overnight. The day after, pulp press water was filtrated away of it and at the same time a cake was prepared of it through filtration and drying. The surface resistivity of the cake was $10 \times 10^3 \Omega$. Washes of the product were continued by elutriating it to water again and by filtration until the pH of washing water was more than 6. This required a total of 10 washes. A cake was prepared of the third wash where the surface resistivity was $10 \times 10^4 \Omega$, as well as of the sixth wash where the surface resistivity of the cake was $10 \times 10^5 \dots 6$.

Microscopic figures have been taken from woodfree pulp of the reaction mixture and the sixth wash (appendix II). Pictures show that the polymer has been well attached to fibres and that it has given the whole fibre a typical green colour of polyaniline and that colour turns blue when the amount of a counter-ion decreases due to washes.

EXAMPLE 16. In presence of ligneous thermomechanical fibre, polymerization of aniline where phenol sulphonic acid is used as a counter-ion. The amount of aniline was 25 % of the amount of fibres.

5 A total of 1000 g of thermomechanical pulp (TMP-reject) that included 7 g of fibre was put in a flask. Then, 5.1 g of 65 % aqueous solution of phenol sulphonic acid and 0.008 g of phenylenediamine were added into pulp. The reaction mixture was mixed for 30 minutes and then, 1.75 g of aniline was added when a water-soluble aniline-phenolsulphonic acid salt was formed and the reaction mixture became yellow bright. The mixture was cooled
10 during blending in an ice-water bath to the temperature of 9°C. Then, 4.6 g of ammonium persulphate was dissolved in 50 ml of water and this solution was added into the reaction mixture during 25 minutes. After addition of ammonium persulphate, blending was continued for 4 hours. At this stage, the product was black and a bit bluish which means that the reaction had ended. The product was left stand overnight. The day after, pulp press
15 water was filtrated away of it and at the same time, a cake was prepared of it through filtration and drying. The surface resistivity of the cake was $10 \times 10^4 \Omega$. Washes of the product were continued by elutriating it to water again and by filtration until the pH of washing water was above 6. This required a total of 6 washes. A cake was prepared of the third wash where the surface resistivity was $10 \times 10^5 \dots 6 \Omega$, as well as of the sixth wash
20 where the surface resistivity of the cake was $10 \times 10^7 \Omega$. Microscopic figures have been taken from woodfree pulp of the reaction mixture and of the sixth wash (Appendix II).

Microscopic pictures show that majority of fibres and of fines has been stained to polyaniline green. However, among these there are fibres where no reaction has happened
25 on their surfaces. These unreacted fibres have anyway been stained into yellow that could tell that aniline-counter-ion salt is attached to them. In any case, the amount of an oxidant has not been sufficient to polymerize the sites in question and hence, the oxidant has been consumed in the reaction mixture in some competing reaction like oxidation of lignin. Due to washes, the counter-ion is washed away from the fibre too and polyaniline dedopes into
30 blue that can be seen from the fibre picture of the sixth wash. However, the colour of the fibre is clearly lighter than the colour of polyaniline attached to the chemical pulp fibre in Example 17.

EXAMPLE 17. In presence of grinded ligneous chemical pulp fibre, polymerization of aniline where phenol sulphonic acid is used as a counter-ion. The amount of aniline was 25 % of the amount of fibres.

5 A total of 100 g of ligneous chemical pulp fibre that included 10 g of fibre was put in a flask. Then, 900 g of water and 7.2 g of 65 % aqueous solution of phenol sulphonic acid were added. The reaction mixture was mixed for 10 minutes and then, 2.5 g of aniline was added when a water-soluble aniline-phenolsulphonic acid salt was formed. At this stage, the mixture was still white. The mixture was cooled during blending in an ice-water bath to
10 the temperature of 9°C. Then, 6.4 g of ammonium persulphate was dissolved in 60 ml of water and this solution was added into the reaction mixture during 35 minutes. After addition of ammonium persulphate, blending was continued for 4 hours. At this stage, the product was black and slightly bluish. The product was left stand overnight. The day after, pulp press water was filtrated away of it and at the same time, a cake was prepared of it
15 through filtration and drying. The surface resistivity of the cake was $10 \times 10^4 \Omega$. Washes of the product were continued by elutriating it to water again and by filtration until the pH of washing water was more than 6. This required a total of 10 washes. A cake was prepared of the third wash where the surface resistivity was $10 \times 10^5 \Omega$, as well as of the sixth wash where the surface resistivity of the cake was $10 \times 10^7 \Omega$. Microscopic figures have been
20 taken of the reaction mixture and of the tenth wash (Appendix II).

Microscopic figures show that the fibres and fines are stained throughout by typical green colour of polyaniline and that the colour is maintained also during washes when the reduction of the surface resistivity depends purely on the dedoping of polyaniline and not
25 on the detachment of polyaniline from the fibre.

EXAMPLE 18. In presence of ligneous thermomechanical fibre, polymerization of aniline where camphor sulphonic acid is used as a counter-ion. The amount of aniline was 25 % of the amount of fibres.

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A total of 1000 g thermomechanical pulp (TMP-reject) that included 10 g of fibre was put in a flask. Then, 4.4 g of camphor sulphonic acid was added when the mixture became maize yellow. The reaction mixture was mixed for 20 minutes and then, 1.75 g of aniline

was added when a water-soluble aniline-camphor sulphonic acid salt was formed and the mixture became yellow bright. The mixture was cooled during blending in an ice-water bath to the temperature of 10°C. Then, 4.6 g of ammonium persulphate was dissolved in 45 ml of water and this solution was added into the reaction mixture during 20 minutes. After addition of ammonium persulphate, blending was continued for 4 hours. At this stage, the product was brown. The product was left stand overnight. The day after, the product was dark green and pulp press water was filtrated away of it. Simultaneously, a cake was prepared through filtration and drying and the surface resistivity of it was $10 \times 10^5 \Omega$. Washes of the product were continued by elutriating it to water again and by filtration until the pH of washing water was more than 6. This required a total of six washes. A cake was prepared of the third wash where the surface resistivity was $10 \times 10^7 \Omega$, as well as of the sixth wash where the surface resistivity of the cake was $10 \times 10^{12} \Omega$. Microscopic figures have been taken of the reaction mixture and of the sixth wash (Appendix II).

Microscopic figures show plenty of blond areas with no polyaniline green colour. Even in the reaction mixture, the colour of fibres/polyaniline is greyish green and after the sixth wash, fibres are observed to be blond aquamarin and there are even more unstained areas. Here, as well as in Example 16, the unstained areas are yellow which refers to that the aniline-counter-ion salt is attached to the fibre, the polymerization being unfinished when the oxidant has been consumed in some competing reaction with lignin.

EXAMPLE 19. In presence of grinded ligneous chemical pulp fibre, polymerization of aniline where camphor sulphonic acid is used as a counter-ion. The amount of aniline was 25 % of the amount of fibres.

A total of 100 g of grinded coniferous chemical pulp fibre that included 10 g of fibre was put in a flask. Then, 6.3 g of camphor sulphonic acid was added. The reaction mixture was mixed for 20 minutes and then, 2.5 g of aniline was added when a water-soluble aniline-camphor sulphonic acid salt was formed. The mixture was cooled during blending in an ice-water bath to the temperature of 8°C. Then, 6.4 g of ammonium persulphate was dissolved in 62 ml of water and this solution was added into the reaction mixture during 30 minutes. After addition of ammonium persulphate, blending was continued for 5 hours. At this stage, the product was black and slightly reddish. The product was left stand overnight.

The day after, pulp press water was filtrated away of the black green mixture and at the same time, a cake was prepared through filtration and drying. The surface resistivity of the cake was $10 \times 10^4 \Omega$. Washes of the product were continued by elutriating it to water again and by filtration until the pH of washing water was more than 6. This required a total of eight washes. A cake was prepared of the third wash where the surface resistivity was $10 \times 10^6 \Omega$, as well as of the sixth wash where the surface resistivity of the cake was $10 \times 10^7 \Omega$. Microscopic figures of the cellulosic pulp have been taken of the reaction mixture and of the sixth wash (Appendix II).

Microscopic figures show that the fibres and fines are stained throughout by typical green colour of polyaniline and that the colour is maintained also during washes when the reduction of the surface resistivity results purely from the dedoping of polyaniline and not on the detachment of polyaniline from the fibre.

EXAMPLE 20. In presence of ligneous thermomechanical pulp, polymerization of aniline where methane sulphonic acid is used as a counter-ion. The amount of aniline was 50 % of the amount of fibres.

A total of 500 g of thermomechanical pulp (TMP/GW) that included 5 g of fibre was put in a flask. Then, 2.6 g of methane sulphonic acid was added. Thereafter, 2.5 g of aniline was added when a water-soluble aniline-methane sulphonic acid salt was formed and the reaction mixture became yellow bright. The mixture was cooled during blending in an ice-water bath to the temperature of 6°C . Then, 6.14 g of ammonium persulphate was dissolved in 60 ml of water and this solution was added into the reaction mixture during 15 minutes. After addition of ammonium persulphate, blending was continued for 3 hours. At this stage, the product was dark orange. The product was left stand overnight. The day after, pulp press water was filtrated away of the black green product. Simultaneously, a cake was prepared through filtration and drying and the surface resistivity of it was $10 \times 10^3 \Omega$. Washes of the product were continued by elutriating it to water again and by filtration until the pH of washing water was more than 6. This required a total of 7 washes. A cake was prepared of the third wash where the surface resistivity was $10 \times 10^5 \Omega$, as well as of the sixth wash where the surface resistivity of the cake was $10 \times 10^6 \dots 7 \Omega$. Microscopic

figures of the cellulosic pulp have been taken of the reaction mixture and of the sixth wash (Appendix II).

Microscopic figures show that fines and part of the fibre are clearly polyaniline green but
 5 part of fibres has stayed yellow i.e. the aniline salt is in the fibre but the reaction has stayed unfinished while lignin has consumed an oxidant before the polymerization of aniline has ended. However, the formed polymer stays well in the fibre during washes and it only dedopes which results in the reduction of surface resistivity in the filter cake.

10 **EXAMPLE 21.** In presence of grinded chemical pine pulp fibre, polymerization of aniline where methane sulphonic acid is used as a counter-ion. The amount of aniline was 25 % of the amount of fibres.

A total of 100 g of thermomechanical pulp (TMP/GW) that included 10 g of fibre was put
 15 in a flask. Then, 900 g of water and 2.6 g of methane sulphonic acid were added in the pulp. Thereafter, 2.5 g of aniline was added when a water-soluble aniline-methane sulphonic acid salt was formed. The mixture was cooled during blending in an ice-water bath to the temperature of 6°C. Then, 6.14 g of ammonium persulphate was dissolved in 60 ml of water and this solution was added into the reaction mixture during 35 minutes. After
 20 addition of ammonium persulphate, blending was continued for 4 hours. At this stage, the product was greenish black. The product was left stand overnight. The day after, pulp press water was filtrated away of the product. Simultaneously, a cake was prepared through filtration and drying. The surface resistivity of the cake was $10 \times 10^4 \Omega$. Washing of the product were continued by elutriating it to water again and by filtration until the pH of
 25 washing water was more than 6. This required a total of 7 washes. A cake was prepared of the third wash where the surface resistivity was $10 \times 10^6 \Omega$, as well as of the sixth wash where the surface resistivity of the cake was $10 \times 10^9 \Omega$.

ELECTRICALLY CONDUCTIVE PAPER SHEETS PRODUCED OF FIBRES

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At TKK (the Techincal University of Helsinki), paper sheets were produced of the samples prepared in accordance with Examples 1 and 2, either directly from treated pulp or by mixing untreated, coniferous cellulosic pulp in it. The sheets were produced by using sheet

preparation standard SCAN-C 26:76. Surface resistivities from both sides of the sheets were measured in KCl by a standard method ASTM D257-93 used for determination of paper resistivity. In the method, the sample is applied between two electrodes. The lower, circular centre electrode is surrounded by another circle electrode, and the surface

5 resistivity is measured from the voltage between the lower centre electrode and the circular electrode while the upper electrode eliminates errors resulting from the perpendicular conductivity of paper. The apparatus was composed of a HP 4339A-type high resistivity meter and of HP 1600B-type measurement geometry. The measurement temperature was 23 °C, the relative humidity of air was 20 % RH, the measurement voltage was 100 V DC

10 and the charging time was 30.0s.

The paper sheet that contained as much polyaniline as chemical pulp fibre and which was prepared directly of sample 1 was too fragile to be a paper. When mixing 50 % of pure chemical pulp fibre in it, a sheet with surface resistivity of level from $10\text{exp}5$ to $10\text{exp}6$

15 Ω/sq was obtained. The surface resistivity rose in the level of $10\text{exp}9$ - $10\text{exp}10$ Ω/sq when the polyaniline treated fibre was mixed with 25 % of pure fibre.

The surface resistivity of a paper sheet, made directly of sample 2 that included 10 % of polyaniline attached to a chemical pulp fibre, was at a level of $10\text{exp}7$ Ω/sq . By adding 50

20 % of pure chemical pulp fibre to this fibre, the surface resistivity of the paper sheet increased to a level of $10\text{exp}10$ Ω/sq (5 % of polyaniline within the fibre).

In addition, paper sheets of samples of examples 4, 5, 6, 7 and 8 were prepared at TKK. Paper sheets were prepared directly from fibre samples of samples 4, 5 and 6, prepared

25 with different counter-ions, by mixing a half of pure fibre into treated chemical pulp fibre.

Paper sheets were prepared of samples 7 and 8 directly from the treated fibre without adding any pure fibre. In these samples, there were 25 % and 30 % of polyaniline within the fibre. During the production of a sheet, however, part of polyaniline was washed out

30 and so the amount of the bound polyaniline was 17 % (sample 7) and 30 % (sample 8).

Surface resistivities were measured from paper sheets at the temperature of 23°C, at the relative humidity of 20 % and the voltage of 100 V. The surface resistivities were measured both from the top of the sheet (ts) and from the bottom of the sheet (bs).

Additionally, the surface resistivity was measured from a sheet made of pure pine cellulosic pulp. The results are presented in Table III where the surface resistivities, measured from paper sheets prepared from chemical pulp fibre treated with polymerized polyaniline, using different counter ions, are showed. A paper sheet made of pure pine
 5 cellulosic pulp was used as a reference.

Before paper sheets were prepared, there has been 5 %, 10 %, 25 % or 50 % of polyaniline within fibres. The measurement voltage has been 100 V and 10 V in two of the measurements. The measurements have been done both from the top of the sheet (ts) and
 10 from the bottom of the sheet (bs). The results present an average from a total of ten measurements except that in the bottom measurement of example 6 + 50 % chemical pulp fibre, there are nine measurements in total.

Table III

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Sample	Ts / top Average Ω / \square	Ts / top Deviation Ω / \square	Bs / bottom Average Ω / \square	Bs / bottom Deviation Ω / \square
Ref_a	6.16E+13	2.88E+13	1.94E+14	1.3E+14
Ref_bc	1.23E+15	2.22E+15	1.33E+15	2.8E+15
Pan-dbsa 5 %, Ex. 4 + 50 % chemical pulp fibre	3.37E+8	2.41E+8	1.29E+9	1.03E+9
Pan-dbsa 10 %, Ex. 4	5.33E+7	1.21E+7	3.74E+7	1.45E+7
Pan-p-tsa 5 %, e.g. 5 + 50 % chemical pulp fibre	8.23E+10	1.17E+10	5.17E+10	1.45E+10
Pan-p-tsa 10 %, Ex. 5	4.08E+9	4.69E+8	2.21E+9	3.22E+8
Pan-sa 5 %, Ex. 6 + 50% chemical pulp fibre	4.26E+14	4.34E+14	2.65E+14	2.53E+14
Pan-sa 10 %, Ex. 6	6.05E+14	5.52E+14	1.3E+15	2.36E+15
Pan-p-tsa 25 %, Ex. 7	6.11E+8	1.18E+8	7.01E+8	9.02E+7
Pan-p-tsa 25 %, Ex. 7, 10 V	5.26E+8	1.2E+8	6.15E+8	6.6E+7
Pan-p-tsa 50 %, Ex. 8, 10 V	3.1E+6	7.27E+5	3.24E+6	4.66E+5

Table III shows that when preparing a paper sheet including polyaniline polymerized with dodecyl benzene sulphonic acid, a proper electrical conductivity can be achieved already
 20 with polyaniline concentration of 5 %. This good electrical conductivity can be utilised especially through a ligneous fibre (e.g. through a thermomechanical pulp) because a proper attachment of dodecyl benzene-acid-polyaniline to this kind of fibre is achieved.

In the presence of p-toluene sulphonic acid, the polymerized polyaniline attached very well to a chemical pulp fibre, hence making the risk of out washing lower. This polyaniline is needed slightly more than dodecyl benzene sulphonic-polyaniline within fibre, preferably 10 % or more, to achieve a proper electrical conductivity in the fibre.

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Therefore, by the aid of the correct fibre type and the polyaniline-counter-ion combination, it is possible to produce electrically conductive chemical pulp fibres of which electrically conductive paper sheets can further be produced.

- 10 In the paper production, however, also the mechanical properties of the finished paper must be considered and therefore, the density (SCAN-P 7:75), the tensile strength (SCAN-P 38:80) and the Scott bond z-strength (method TAPPI T 569 pm-00) were determined. The results of mechanical properties are presented in Table IV.

15 **Table IV**

	Density kg/m ³	Tensile index, Nm/g	Scott bond z- strength J/m ²	Surface resistivity, Ohm/
<u>Coniferous cellulosic pulp reference, example 1</u>	676	67.8	356	6.20E+13
25% aniline of paper (dbsa), Example 1	631	44.1	146	3.40E+08
50% aniline of paper (dbsa), Example 1	656	37.5	114	5.30E+07
<u>Coniferous cellulosic pulp reference, Examples 5 and 6</u>	638	76.5	271	1.20E+15
10% aniline of paper (p-TSA), Example 5	579	46.5	214	4.10E+09
10% aniline of paper (citric acid), Example 6	588	47.8	214	6.10E+14
<u>Coniferous cellulosic pulp reference, Examples 7 and 8</u>	676	67.8	356	6.30E+13
25% aniline of paper (p-TSA), Example 7	502	42.2	244	5.60E+08
50% aniline of paper (p-TSA), Example 8	477	34.2	161	3.10E+06

In the production of the sheets, it was noticed that when using dodecyl benzene sulphonic acid as a counter-ion the retention of polyaniline to paper was weak. This was seen as intensively mottled colour of the sheet, among other things. When using p-toluene sulphonic acid or citric acid, instead, this kind of a problem was not observed.

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Table 2 shows that clearly lower paper resistivity is achieved by using p-toluene sulphonic acid as a counter-ion with a dose of 10 % than that by using citric acid.

10 It can be seen from the results that with all counter-ions used, the attachment of paper and thereby the strengths (tensile index and Scott bond) reduce clearly in comparison with the reference sample without any polyaniline.